# COMPONENTS: 1. Cobalt selenite; CoSeO<sub>3</sub>; [10026-23-0] Ripan, R.; Verıceanu, G. 2. Water; H<sub>2</sub>O; [7732-18-5] Studia Univ. Babes-Bolyai, Ser. Chim. 1968, 13, 31-37. VARIABLES: One temperature: 291 K Mary R. Masson

## EXPERIMENTAL VALUES:

All concentrations are expressed in units of mol  $dm^{-3}$ .

Concentration	$_{\text{mol}}^{K}$ sO $_{\text{mol}}^{2}$ dm $^{-6}$	Mean K <sub>sO</sub>	$^{pK}$ s0
3.160 x 10 <sup>-4</sup> 3.310 x 10 <sup>-4</sup> 3.425 x 10 <sup>-4</sup> 3.511 x 10 <sup>-4</sup> 3.564 x 10 <sup>-4</sup> 3.528 x 10 <sup>-4</sup>	0.999 x 10 <sup>-7</sup> 1.095 x 10 <sup>-7</sup> 1.173 x 10 <sup>-7</sup> 1.233 x 10 <sup>-7</sup> 1.270 x 10 <sup>-7</sup> 1.245 x 10 <sup>-7</sup>	$1.2 \pm 0.2 \times 10^{-7}$ $mol^2 dm^{-6}$	6.92

The concentration c in the saturated solution was calculated from the measured conductivity  $\kappa$  from the equation

$$c = \frac{1000\kappa}{\Lambda^{\circ}}$$

#### Compiler's note

Neither in the determination of the ionic conductivity of the selenite ion nor in the evaluation of the solubility product was hydrolysis of the selenite ion taken into account. This would give rise to errors, since, for example, in a 0.001M solution,  $[Se0\frac{3}{3}] = 0.000955M$ ,  $[HSe0\frac{3}{3}] = 0.000045M$  and  $[OH^-] = 0.000045M$ , and hydroxide and hydrogen selenite have different ionic conductivities from selenite. If the ionic conductivity of hydrogen selenite were known, the experimental results could have been interpreted correctly (cf. ref. 2), but this value does not seem to be available.

However, because the calibration and sample solutions had concentrations of about the same order of magnitude, the errors would cancel to some extent, but the  $K_{\rm SO}$  value cannot be regarded as reliable.

#### AUXILIARY INFORMATION

## METHOD APPARATUS/PROCEDURF:

The ionic conductivity of the selenite ion in water was determined by measuring the mean molar conductivities of a series of aqueous solutions of lithium selenite with concentrations below 2 x  $10^{-3} \mathrm{mol}$  dm $^{-3}$ . The mean molar conductivity at infinite dilution was found by extrapolation to be  $172~^{\pm}~2.9~\Omega^{-1}\mathrm{cm}^2\mathrm{mol}^{-1}$  at 18°C. At that temperature, the ionic conductivity of the lithium ion is  $33.4~\Omega^{-1}\mathrm{cm}^2\mathrm{mol}^{-1}$ , so the ionic conductivity of the selenite ion is  $105.2~\Omega^{-1}\mathrm{cm}^2\mathrm{mol}^{-1}$ .

The well washed cobalt selenite was mixed with 150 ml of water and agitated intermittently for 1 hr. From this, 10-20 ml was taken in the conductivity cell and the conductivity measured. The sampling and measurement were repeated until a constant value for the conductivity was obtained.

The value of  $\Lambda^\circ$  =  $(\lambda_+ + \lambda_-),$  the molar conductivity, was calculated with  $\lambda_-$  = 105.2 and  $\lambda_+$  = 90  $\Omega^{-1} {\rm cm}^2 {\rm mol}^{-1}$ .

## SOURCE AND PURITY OF MATERIALS:

Lithium selenite was prepared from sublimed selenium dioxide by neutralization with lithium hydroxide. An approximately 0.05M solution was standardized gravimetrically, and this was used to prepare the various dilutions.

The composition of the selenite was checked by analysis.

#### ESTIMATED ERROR:

Temperature:  $\pm 0.5 \text{ K}$ Error in  $K_{s0}$  (2s) = 0.2 x  $10^{-7}$  (compiler)

## REFERENCES:

- 1. Landolt-Bornstein Physicalisch-Chemische Tabellen II 1923, p. 1105.
- 2. Monk, C.B. J. Chem. Soc. 1949, 429.

## COMPONENTS:

- Cobalt(II) selenite; CoSeO<sub>3</sub>; [10026-23-0]
- 2a. Nitric acid; HNO3; [7697-37-2]
- 2b. Sulfuric acid; H<sub>2</sub>SO<sub>4</sub>; [7664-93-9]
- 3. Water; H<sub>2</sub>O; [7732-18-5]

## ORIGINAL MEASUREMENTS:

Chukhlantsev, V.G.; Tomashevsky, G.P.

Zh. Anal. Khim. 1957, 12, 296-301; \*J. Anal. Chem. USSR 1957, 12, 303-9.

#### VARIABLES:

VARIABLES:

Nitric and sulfuric acid concentrations One temperature: 293 K

#### PREPARED BY:

Mary R. Masson

#### EXPERIMENTAL VALUES:

All concentrations are expressed in units of mol  $dm^{-3}$ .

HII Concentrations are improved in an area							
Soln.	Initial pH	Final pH	[Co <sup>2+</sup> ]	рСо	$\log \alpha_{L(H)}$	p[SeO3 <sup>2-</sup> ]	pK <sub>s</sub> 0
нио3	2.41	5.69	$7.8 \times 10^{-3}$	2.11	2.30	4.41	6.52
	2.06	4.20	$3.5 \times 10^{-2}$	1.46	3.80	5.26	6.72
н <sub>2</sub> so <sub>4</sub>	2.74	6.39	$2.0 \times 10^{-3}$	2.70	1.60	4.30	7.00
	2.13	4.30	$2.1 \times 10^{-2}$	1.68	3.70	5.38	7.06
	2.08	4.25	$2.7 \times 10^{-2}$	1.57	3.75	5.32	6.89

The average value is  $K_{s0} = 1.6 \times 10^{-7} \text{ mol}^2 \text{dm}^{-6}$ .  $(pK_{s0} = 6.8)$ 

#### Notes.

[Se<sub>tot</sub>] = [Co<sup>2+</sup>] and [SeO<sub>3</sub><sup>2-</sup>] = [Se<sub>tot</sub>]/ $\alpha$ <sub>L(H)</sub> where  $\alpha$ <sub>L(H)</sub> = (1 + [H<sup>+</sup>]/K<sub>2</sub> + [H<sup>+</sup>]<sup>2</sup>/K<sub>1</sub>K<sub>2</sub>) and the acid dissociation constants have the values K<sub>1</sub> = 4 x 10<sup>-3</sup> and K<sub>2</sub> = 1.0 x 10<sup>-8</sup> (ref. 1).

## AUXILIARY INFORMATION

#### METHOD APPARATUS/PROCEDURE:

Solutions of nitric and sulfuric acid were saturated with cobalt selenite by shaking in a thermostat at  $20^{\pm}0.05^{\circ}\text{C}$  for 8 hr. The remaining solid phase was removed by centrifugation, then the pH was measured ("Moskip" pH meter, to 0.01 pH unit) and the cobalt concentration was determined by gravimetry of the sulfate.

## SOURCE AND PURITY OF MATERIALS:

C.P.-grade reagents were used. Cobalt selenite was prepared by adding 0.1N sodium selenite (a 3% excess) to 0.1N cobalt nitrate at  $50-60^{\circ}\mathrm{C}$ . After prolonged standing, the precipitate was separated by centrifugation and decanting, then it was dried at  $40^{\circ}\mathrm{C}$ . Cobalt was determined gravimetrically as the sulfate, and selenium as the element.

# ESTIMATED ERROR:

 $\pm 0.8 \times 10^{-7}.$  (The spread in the results is 0.64 of a log unit.) Temperature:  $\pm 0.0 \ \text{K}$ 

### REFERENCES.

1. Rumpf, P. Compt. Rendu 1933, 197, 686.

## COMPONENTS:

 Cobalt selenite; CoSeO<sub>3</sub>; [10026-23-0]

2. Water; H<sub>2</sub>O; [7732-18-5]

## ORIGINAL MEASUREMENTS:

Pyatnitskii, I.V.; Durdyev, M.

*Ukr. Khim. Zh.* 1966, 32, 77-81. \*(English translation, pp. 57-61.)

#### VARIABLES:

One temperature (room?) pH varied

PREPARED BY:

Mary R. Masson

#### EXPERIMENTAL VALUES:

[CoSeO <sub>3</sub> ]	pН	[Co <sup>2+</sup> ] x 10 <sup>4</sup> mol dm <sup>-3</sup>	αL(H)	$[SeO_3^{2-}]$ x $10^5$ mol dm <sup>-3</sup>	$K_{\rm s0} \times 10^8$ $mo1^2 dm^{-6}$
0.037	7.55	1.99	3.45	5.77	1.15
0.031	7.65	1.67	2.95	5.66	0.945
0.034	7.60	1.83	3.19	5.73	1.05

Mean 
$$K_{sO} = 1.05 \times 10^{-8} \text{ mol}^2 \text{ dm}^{-6}$$
  
 $pK_{sO} = 7.98$ 

Columns 1 and 2 give data from the original paper; the other data were calculated by the compiler, since there appeared to be errors in the original calculations.

## AUXILIARY INFORMATION

## METHOD APPARATUS/PROCEDURE:

Small quantities of cobalt selenite were placed in a flask, water was added, and the flask was shaken until equilibrium was reached (2 hr). Cobalt in the filtrate was determined photometrically with nitroso-R-salt, and the pH of the solution was measured (LP-58 pH meter).

The solubility measurements appear to have been made at room temperature.

# SOURCE AND PURITY OF MATERIALS:

Cobalt selenite dihydrate was prepared by adding a slight excess of sodium or ammonium selenite to a solution of cobalt sulfate. The precipitate was heated at 60°C for 1 hr, then filtered off after 3-4 hr. It was dried at 105-110°C.

#### ESTIMATED ERROR:

The spread in the  $K_{\rm s0}$  results is 0.2 x  $10^{-8}$ .

## REFERENCES:

#### COMPONENTS:

- 1. Cobalt selenite; CoSeO3; [10026-23-0]
- 2. Ammonium selenite; (NH<sub>4</sub>)<sub>2</sub>SeO<sub>3</sub>;
- [7783+19-9]
- 3. Potassium nitrate; KNO3; [7757-79-1]
- 4. Water; H<sub>2</sub>O; [7732-18-5]

# ORIGINAL MEASUREMENTS:

Pyatnitskii, I.V.; Durdyev, M.

*Ukr. Khim. Zh.* 1966, 32, 77-81. (English translation, pp. 57-61.)

## VARIABLES:

One temperature (room?)

pH and selenite concentration varied

#### PREPARED BY:

Mary R. Masson

#### EXPERIMENTAL VALUES:

All concentrations are expressed in units of mol  $dm^{-3}$ .

Solubility data for ionic strength 0.3 mol  $\mathrm{dm}^{-3}$ 

[CoSeO3]	[Se03 <sup>2</sup> -]	$K_{s0} \times 10^{6}$	
x 10 <sup>4</sup>	$\times 10^{2}$	$mo1^2 dm^{-6}$	$[SeO_3^{2-}]$ for minimum solubility = 0.023
1.71	0.56	0.91	
1.51	1.15	1.38	$K_{\text{instab}} = ([SeO_3^{2-}]_{\min})^2$
1.37	2.30	1.58	_
1.49	4.60	1.37	$= 5.3 \times 10^{-4}$
1.83	9.20	0.99	
2.81	18.4	0.79	

Mean  $K_{s0} = 1.17 \times 10^{-6} \text{ (pK}_{s0} = 5.93)$ 

Solubility data for ionic strength 0.01 mol  ${\rm dm}^{-3}$ 

i	pН	[CoSeO <sub>3</sub> ]	$[Se0_3^{2-}]$	$K_{s0} \times 10^{7}$	
	1	x 10 <sup>4</sup>	$\times 10^{3}$	$mo1^2 dm^{-6}$	2
	8.25	1.19	1.0	1.02	$[SeO_3^{2-}]$ for minimum solubility = 2.5 x $10^{-3}$
	8.4	1.05	1.95	1.23	4
	8.45	1.05	2.9	1.29	$K_{\text{instab}} = 6.25 \times 10^{-6}$
	8.55	1.19	3.9	1.35	_
	8.55	1.15	4.8	1.18	Mean $K_{s0} = 1.14 \times 10^{-7}$
	8.55	1.24	5.7	1.14	
	8.55	1.36	6.7	1.12	$(pK_{s0} = 6.94)$
	8.55	1.42	7.7	1.04	
	8.55	1.52	8.6	1.02	
	8.55	1.73	9.6	1.05	

## AUXILIARY INFORMATION

## METHOD APPARATUS/PROCEDURE:

Solids and solutions were equilibrated in flasks with shaking for 2 hr. Cobalt in the filtrate was determined with nitroso-R-salt photometrically, and the pH was measured (LP-58 pH meter). The measurements appear to have been made at room temperature.

The solubility product values were calculated from the formula:

$$K_{s0} = \frac{[\text{Co}^{2+}].K_{instab}.[\text{Se0}_{3}^{2-}]}{K_{instab} + [\text{Se0}_{3}^{2-}]^{2}}$$

Compiler's note: these two sets of results do not appear to be consistent with each other or with the water solubility data. Minor corrections to the calculations made no significant difference, so the authors' original figures are reproduced. The differences appear rather large to be caused simply by the ionic-strength effect.

## SOURCE AND PURITY OF MATERIALS:

Cobalt selenite dihydrate was prepared by adding a slight excess of sodium or ammonium selenite to a solution of cobalt sulfate. The precipitate was heated for 1 hr at 60°C, then filtered off after 3-4 hr. It was dried at 105-110°C.

# ESTIMATED ERROR:

At 
$$I = 0.3$$
,  $s = 0.3 \times 10^{-6}$  for  $K_{s0}$   
At  $I = 0.01$ ,  $s = 0.12 \times 10^{-7}$  for  $K_{s0}$ 

## REFERENCES: